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(54) **LIQUID GLYCOL BENZOATE COMPOSITIONS AND POLYMER COMPOSITIONS CONTAINING SAME**

FLÜSSIGE BENZOATZUSAMMENSETZUNGEN UND SELBIGE ENTHALTENDE
POLYMERZUSAMMENSETZUNGEN

COMPOSITIONS DE BENZOATE LIQUIDE ET COMPOSITIONS POLYMERES LES RENFERMANT

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EP 1 000 009 B1

Description

[0001] This invention relates to liquid ester compositions. More particularly, this invention relates to mixtures of esters derived from certain aromatic monocarboxylic acids and specified combinations of oligomeric and optionally monomeric ethylene glycols. These mixtures are liquids at temperatures below the freezing point of the individual constituent esters.

DESCRIPTION OF THE PRIOR ART

[0002] Esters derived from 1) benzoic or toluic acid and 2) an aliphatic glycol or oligomer thereof together with methods for preparing these esters are described in the prior art.

[0003] Certain of these esters, particularly esters derived from glycols containing from 2 to about 9 carbon atoms, constitute a preferred class of plasticizers for polyvinyl chloride and other inherently rigid organic polymers because of the ability of the esters to improve the processability of the rigid polymers without adversely affecting their desirable physical properties.

[0004] United States Patent No. 4,656,214, which issued to Wickson on April 7, 1987 describes diesters of 1) linear glycols containing from 2 to 8 carbon atoms, 2) a first carboxylic acid of the formula $R^1R^2R^3C(O)OH$ and 3) a second carboxylic acid of the formula $R^5C(O)OH$, wherein R^1 and R^2 are individually selected from alkyl containing from 1 to 4 carbon atoms, R^3 is hydrogen or alkyl from 1 to 6 carbon atoms, R^5 is selected from the group consisting of phenyl, mono- di- and trialkyl-substituted phenyl containing from 9 to 12 carbon atoms and $-(CH_2)_nPh$ where Ph is phenyl and the value of n is from 1 to 6, inclusive. The esters contain from 16 to 19 carbon atoms and are useful as strain-resistant plasticizers for polyvinyl chloride.

[0005] The use as plasticizers of esters derived from benzoic acid and a polyhydric alcohol is described from benzoic acid and a polyhydric alcohol is described in Japanese Laid Open Patent Application No. 54/18859, published on February 13, 1979.

[0006] Published European Patent Application No. 244,107, issued on November 4, 1987 describes plasticizers compositions for elastomers comprising I) a trimellitate ester, II) a saturated linear dicarboxylate ester obtained by reacting 1) a dicarboxylic acid with at least one monohydric alcohol or 2) an aliphatic monocarboxylic acid with at least one of diethylene glycol, triethylene glycol and tetraethylene glycol, and III) a dialkyl ester of a thiodicarboxylic acid.

[0007] U.S. Patent No. 4, 444,933 to J. Anderson and P. Columbus describes cyanoacrylate adhesives containing a plasticizer that is selected from dipropylene glycol dibenzoate, diethylene glycol dibenzoate, a mixture of the foregoing two compounds, butylbenzyl phthalate, dibutyl phthalate or a benzoate ester of di- or polyhydroxy branched aliphatic compounds.

[0008] Research Disclosure No. 17943, published on March 10, 1979 describes plasticized road marking compositions containing from 10 to 50 weight percent of a plasticizer described as a benzoic acid ester exemplified by glyceryl tribenzoate, neopenyl dibenzoate, tribenzoate or a polyester.

[0009] GB 496 574, US 2,283,192 and US 5,545,472 disclose diethylene glycol dibenzoate and triethylene glycol dibenzoate with possible other esters, and their use as plasticizers.

[0010] Esters derived from benzoic acid and either di- or triethylene glycol are particularly desirable because of the wider availability and lower cost of these glycols relative to the corresponding propylene glycols. One of the disadvantages of using benzoic or toluic acid esters of ethylene glycol, di- and triethylene glycol as plasticizers is that these esters are solids at 25°. Polymer compositions containing these esters as additives typically require heating to at least the melting point of the additive to uniformly blend the additive into the composition.

SUMMARY OF THE INVENTION

[0011] The present invention is based on the discovery that within a relatively limited range of proportions blends containing the di- and triethylene glycol esters of benzoic and toluic (methylbenzoic) acids are liquids below the freezing point of the individual constituent esters.

[0012] When the present blends are used as plasticizers they can optionally include at least one additional ester that is a liquid at 25°C and is conventionally used as a plasticizer for organic polymers. The additional liquid ester(s) increases the relative concentration of triethylene glycol ester relative to diethylene glycol ester that can be present in a composition that is liquid below the freezing points of both glycol esters.

DETAILED DESCRIPTION OF THE INVENTION

[0013] This invention provides liquid ester compositions comprising a mixture of:

- 1) a first diester of the formula $ArC(O)(OCH_2CH_2)_2O(O)Car$, and

2) a second diester of the formula $\text{ArC(O)(OCH}_2\text{CH}_2)_3\text{O(O)CAr}$; wherein Ar represents a phenyl or methylphenyl radical, the weight ratio of said first diester to said second diester is from 1.22:1 to 9:1, and the freezing point of said mixtures are below the freezing points said first and second diesters.

[0014] In preferred embodiments the first and second diesters preferably constitute at least 50 weight percent of the present liquid ester composition. The remaining ingredients of these preferred embodiments are esters exhibiting freezing points below 25° C. These additional esters are derived from mono- or polyhydric alcohols and aromatic or aliphatic mono- and/or dicarboxylic acids. The presence of these additional liquid esters increases the concentration of the triethylene glycol diester relative to the diethylene glycol diester that can be present in compositions that are liquid below the freezing point of these glycol diesters.

[0015] Examples of the additional liquid esters that can be present in the ester compositions of the present invention include but are not limited to 1) diesters derived from benzoic acid and diols containing from 3 to 10 carbon atoms, 2) esters derived from benzoic acid and monohydric alcohols containing from 4 to 12 carbon atoms, 3) aliphatic esters of the formula $\text{R}^1\text{O(O)C(CH}_2)_m\text{C(O)OR}^1$, and 4) esters derived from phthalic acid and alcohols containing from 4 to 12 carbon atoms. In the preceding formula R^1 is an alkyl individually selected from the group consisting of alkyl and aryl radicals containing from 4 to 12 carbon atoms, and m represents an integer from 2 to 8. The combined weight of these additional plasticizers can constitute up to 50, and preferably from 10 to 35 weight percent of the present liquid ester composition. It will be understood that suitable diols can contain hetero atoms such as oxygen in the hydrocarbon chain.

[0016] Specific examples of additional liquid esters that can be present in the ester compositions of the present invention include but are not limited to propylene glycol and dipropylene glycol dibenzoates, neopentyl glycol dibenzoate, dialkyl adipates, glutarates, azelates and sebacates, isodecyl benzoate and butyl benzyl phthalate.

[0017] The additional liquid esters described in the preceding paragraphs can constitute up to 50 weight percent of the present liquid ester compositions. The presence of these optional liquid esters reduce to about 0.5:1 the weight ratio of the present diethylene glycol benzoate or toluate to triethylene glycol benzoate or toluate required to yield a liquid ester composition at 28°C.

[0018] The present invention also provides compositions comprising 1) an organic polymer such as polyvinyl chloride and 2) up to about 60 weight percent of the present liquid ester compositions as plasticizers. The ester compositions can also be included as plasticizing additives in liquid compositions such as oils and lubricants.

[0019] The novelty of the present ester compositions resides in the lower freezing point of the compositions relative to the freezing temperatures of the two required diesters that constitute at least 50 percent by weight of these compositions. For example, diethylene glycol dibenzoate freezes from 28-29° C, and triethylene glycol dibenzoate freezes from 46-48°C. Unexpectedly, all of the present ester compositions are liquids below 28° C. The actual freezing point of any specific ester composition will be determined by the relative concentrations of the constituent esters.

The Aromatic Carboxylic Acid

[0020] Aromatic carboxylic acids suitable for preparing the present liquid ester compositions can be represented by the general formula ArC(O)OH , wherein Ar represents a phenyl or methylphenyl radical.

The class of carboxylic acids includes benzoic acid and the isomeric toluic acids. It will be understood by those skilled in the art that the corresponding anhydrides and acyl halides can be used in places of the carboxylic acids.

The Glycol Mixture

[0021] The alcohol portions of the solid esters of the present compositions are derived from diethylene glycol and triethylene glycol.

[0022] The relative concentrations of the esters derived from each of the two required oligomeric ethylene glycols used to prepare the present compositions is critical to obtaining compositions that are liquid below 28° C. The ester derived from diethylene glycol constitutes from 55 to 90 weight percent, preferably from 55 to 65 weight percent of the mixture of esters derived from di- and triethylene glycol.

[0023] The present ester compositions can be obtained by first preparing each of the esters individually using any of the known methods for preparing this class of compounds. Following purification the esters are melted prior to or after being combined in the desired proportions.

[0024] In accordance with a preferred method, the present ester compositions are prepared in situ by reacting benzoic acid or one of the isomeric toluic acids with a mixture of diethylene glycol and triethylene glycol. The relative concentration of each glycol is calculated to yield an ester composition within the scope of the present invention, assuming that substantially all of the glycols react with the acid.

[0025] Other glycols such as ethylene glycol, propylene glycol and dipropylene glycol can be included in the mixture

of glycols used to prepare the present ester compositions, so long as the presence of these additional glycols does not detract from the objectives of the present invention.

[0026] Reaction conditions and apparatus required to prepare esters from the corresponding carboxylic acid(s) and mono- or polyhydric alcohol(s) are sufficiently well described in the prior art that a detailed description in the present specification is not required. As taught hereinbefore, the corresponding acyl halides or anhydrides can be used in place of the acid. Reactions using these alternative reactants are described in the prior art.

[0027] To accelerate formation of the present ester compositions, the reaction mixture containing the benzoic or toluic acid and mixture of glycols is preferably heated to the boiling point while the water formed as a by-product is continuously removed by distillation from the reaction mixture. Catalysts such as mineral acids and alkyl titanates can be present in the reaction mixture, and a low boiling hydrocarbon such as hexane can be present in the reaction mixture to facilitate removal of the water.

[0028] The esters can be purified by neutralization of and acid catalysts and/or removal of volatile impurities under reduced pressure.

Use of the Present Liquid Ester Compositions as plasticizers for Organic Polymers

[0029] The liquid ester compositions of the present invention are particularly useful as plasticizers to improve the processability and physical properties of both rigid and non-rigid organic polymers.

[0030] Polymers preferred for use with the present ester composition include polyvinyl chloride and copolymers derived from vinyl chloride and at least one additional copolymerizable mono- or diolefinically unsaturated compounds, including but not limited to vinylidene chloride, vinyl esters of carboxylic acids such as vinyl acetate, and vinyl propionate, esters of ethylenically unsaturated acids such as the alkyl acrylates and -methacrylates. Preferably at least 70 percent of the repeating units of these copolymers are derived from vinyl chloride.

[0031] When used as plasticizers, the present ester compositions can be used alone or in combination with one or more plasticizers known to those skilled in the art to achieve a desired combination of processability and properties in the final polymer composition.

[0032] The concentration of plasticizer(s) in any given polymer composition can vary widely, based on the desired properties and intended use of the composition. Concentrations of from 1 to 200 parts of plasticizer per hundred parts by weight of resin (phr) have been reported, however this range is preferably from 10 to 100 phr.

[0033] The types of polymer compositions into which the present liquid ester compositions can be advantageously incorporated as additives include but are not limited to vinyl flooring laminates, latex caulks, adhesives, coating compositions that are applied as liquids or finely divided solids, and inks.

[0034] The ester compositions of this invention are also useful as seal-swelling additives for oils and lubricants.

[0035] The preparation and use of the liquid ester compositions of this invention are described in detail in the following examples, which should not be interpreted as limiting the scope of the invention described in the accompanying claims.

Example 1

[0036] Ester compositions were prepared by combining in glass containers solid diethylene glycol benzoate (DEGB) and triethylene glycol benzoate (TEGB) in the proportions listed in Table 1. Each of the resultant mixtures weighed ten grams and was heated in an oven maintained at a temperature of 80° C for a period of time sufficient to form a liquid. Each of the liquid compositions was then placed for 24 hours in a freezer maintained at a temperature of -12° C. After 24 hours the containers were examined for evidence of crystallization. The compositions of each sample and the results of the examination are recorded in Table 1.

Table 1

Weight Percent		
DEGDB	TEGDB	Physical State at -12° C
100	0	Solid (c)
0	100	Solid (c)
75	25	Liquid
65	35	Liquid
55	45	Liquid
90	10	Liquid

c = Comparative Example

Example 2Polyvinyl Chloride Resilient Flooring

[0037] This example demonstrates the use of the present ester compositions as plasticizers for resilient flooring applications. Resilient flooring generally consists of at least layers of a vinyl polymer plastisol on a dimensionally stable substrate. The plastisol used as the top layer is clear and provides wear resistance. The next layer is a vinyl foam prepared using a plastisol containing a chemical blowing agent. Plasticizers that are used are selected for this application are required to be effective, stable, provide stain resistance and processability.

[0038] A blend of diethylene glycol dibenzoate, triethylene glycol dibenzoate and di-2-ethylhexyl adipate in the weight ratio of 1.0 to 0.55 to 0.27, referred to below as blend A, was tested in resilient flooring laminates.

[0039] Tables 2 to 4 list the formulations evaluated. The formulations were prepared by mixing the ingredients on a low speed, high intensity mixer and aegassing. The foam layer was coated onto a ceramic felt backing and gelled at 130°C for one minute in a Mathus oven. The top layer was then applied and the construct was fused at 190°C for one and a half minutes. Tables 4 to 8 list the property data obtained from the constructs prepared.

Table 2
Top Coat Formulation

Ingredient	Identification	Manufacturer	Parts By Weight
GEON 173	PVC Dispersion Resin	GEON	100
Plasticizer	Blend A	Present Invention	36
Diluent Plasticizer	Isodecyl benzoate	Velsicol	12
PEG 400 Monolaurate	Polyethylene glycol 400 molecular weight monolaurate	Stepan	1.4
Therm-Chek 1776	Mixed metal stabilizer	Ferro	3.0
Stabilizer	Epoxidized soy bean oil	Velsicol	2.0

Table 3
Foam Layer Formulation

Ingredient	Identification	Manufacture	Parts By Weight
GEON 121 A	PVC dispersion resin	GEON	68.8
GEON 217	PVC blending resin	GEON	31.2
Plasticizer	Blend A	-----	24.3
Diluent Plasticizer	Isodecyl benzoate	Velsicol	19.4
AZO Dispersion (Table 3)	Azodicarbonamide dispersion	-----	12.8
PEG 400 Monolaurate	Polyethylene glycol 400 molecular weight monolaurate	Stepan	1.5
Atomite	Calcium Carbonate	E.C.C.	14.8

Table 4
AZO Dispersion Formulation
 (For Use in Table 3)

Ingredient	Identification	Manufacturer	Parts By Weight
Plasticizer	Blend A	-----	36.4
Diluent Plasticizer	Isodecyl benzoate	Velsicol	12
PEG 400 Monolaurate	Polyethylene Glycol 400 molecular weight monolaurate	Stepan	1.0
CELLOGEN AZ, 3990, azodicarbon-amide	Blowing agent	Uniroyal Chemical	13.2
Asaco AZO 77S, Zinc Oxide	Activator	Asaco	3.2
TiPure R-900 TiO ₂	Pigment	Dupont	26

Table 5
Resilient Flooring Screen Data
Top Coat Plastisol

Test Parameter	
Brookfield RVT Low Shear Viscosity, 23° C, ASTM D-1824	
Initial and 2 hours, Pa.s	
2.5 RPM	5.3
20 RPM	3.7
24 Hours, Pa.s	
2.5 RPM	6.5
20 RPM	4.5
3 Days, Pa.s	
2.5 RPM	9.6
20 RPM	6.2
Ratio of 3 Day/Initial Viscosity	
2.5 RPM	1.8
20 RPM	1.7
High Shear Viscosity, Pa.s, ASTM D-1823, 23° C, @	
10 psi (69 Kpa)	5.2
40 psi (276Kpa)	12.6
70 psi (483Kpa)	17.6
100 psi (689 Kpa)	20.7

Table 6

Resilient Flooring Screen Data
Foam Layer Plastisol

Test Parameter	
Brookfield RVT Low Shear Viscosity, 23° C, ASTM D-1824	
Initial and 2 hours, Pa.s	
2.5 RPM	8.8
20 RPM	5.4
24 Hours, Pa.s	
2.5 RPM	9.8
20 RPM	5.8
3 Days, Pa.s	
2.5 RPM	16.3
20 RPM	7.1
Ratio of 3 Day/Initial viscosity	
2.5 RPM	1.9
20 RPM	1.3
High Shear Viscosity, Pa.s, 23° C, ASTM D-1823	
10 psi (69 Kpa)	4.9
40 psi (276Kpa)	10.5
70 psi (483Kpa)	13.8
100 psi (689 Kpa)	15.3
Foam Blow Ratio (Final thickness to initial thickness prior to fusion)	3.8/1
Foam Blown quality, visual assessment	Pair

Table 7
Resilient Flooring Screen Data Construct
(Top Over Foam)

Test Parameter	
Stain Resistance, Visual and Instrumental reading	
Oil Brown Dye, 1% Soln (0 = best and 10 = worst)	5
Initial Rating, ΔE	9.9
Aged @ 70° C	
1 Week, ΔE	4 (8.5)
2 Weeks, ΔE	5 (7.4)
3 Weeks, ΔE	3 (5.8)
4 Weeks, ΔE	2 (3.6)
Brown Polish, (B)	6 (55.2)
Mustard	0
Black Marker, (ΔE)	6 (25)
Vinyl Heat Stability, 200° C, visual estimate to total discoloration, %	
Rating after 2.5 min.	5
Rating after 5 min	15
Rating after 7.5 min.	30
Rating after 10 min.	60
Rating after 12.5 min.	100

Table 8
Resilient Flooring Screen Data
Laminate (Top Over Foam)

Test Parameter	
Heat Resist., 70° C, Int. ΔE (Against standard white plate)	12.2
ΔE , 1 week	25.8
ΔE , 2 week	30.9
ΔE , 3 week	33.9
UV Light Resistance (Atlas UV chamber)	
ΔE after, Initial (Against standard white plate)	18.3
100 hours	12.2
200 Hours	12.3
300 Hours	11.5
400 Hours	15.2
500 Hours	17.0

The data in the preceding tables demonstrate that blend A is an effective plasticizer for resilient flooring applications.

Example 3

[0040] This example demonstrates the utility of the present liquid ester compositions in compositions intended for use as latex caulk. This type of caulk is used to seal cracks and fill gaps in new and existing residential and commercial buildings. A caulk consists basically of a polymeric binder and fillers. Compatible plasticizers are used in caulks to

increase polymer solids and flexibility, improve adhesion and low temperature performance without adversely affecting storage stability or application properties of the formulation. A liquid ester composition of the present invention containing diethylene glycol dibenzoate, triethylene glycol dibenzoate and dipropylene glycol dibenzoate in the weight ratio of 1 : 0.5 : 0.5, referred to hereinafter as blend B, was incorporated into a latex caulk formulation to determine the utility of the present ester compositions for this application.

To function effectively a plasticizer must be compatible with the base polymer. To determine the compatibility of blend B with a convention caulk polymer, a blend of a caulk polymer emulsion and blend B was prepared using the types and amounts of ingredients listed in Table 9.

[0041] A compatible plasticizer should increase the viscosity of the emulsion. Data in Table 10 demonstrate that blend B increased the viscosity of the base emulsion. To further evaluate the compatibility of blend B with the caulk polymer, a 0.006 inch (0.15mm) thick film of the caulk formulation was applied to a glass plate using a draw down bar and allowed to dry for twenty four hours. The data in Table 11 demonstrate that the film was clear and tacky, which is indicative of compatibility between the caulk formulation and the plasticizer.

[0042] Blend B was incorporated into a typical latex caulk formulation. The ingredients listed in Table 12 were mixed in a low speed, high intensity mixer. The stability, adhesions, tensile strength and hardness of the caulk formulation were determined, and the data summarized in Tables 13 and 14. These data demonstrate that Blend B, a liquid ester composition of the present invention, functions well as a plasticizer for latex caulks.

Table 9

Caulk Polymer/Plasticizer Compatibility Data: Formulation

Ingredient	Parts by Weight, Wet	Parts by Weight, Dry
Caulk Emulsion	100	100
Triton X-405	27.5	50.1
Blend B (plasticizer)	1.7	3.1

Table 10
Compatibility Data of Blend B With Rhoplex(R) 1785

Compatibility	
@ RT Storage	
Initial 1 Day	
Appearance	Clear
Tack	High
7 Day	
Appearance	Clear
Tack	High
28 Day	
Appearance	Clear
Tack	High
@ 50°C Storage	
1 Day	
Appearance	Clear
Tack	High
7 Day	
Appearance	Clear
Tack	High
28 Day	
Appearance	Clear
Tack	High

Note: The plasticizer was incorporated into the base emulsion at a level of 27.5 parts into 100 parts of the wet emulsion with 1.65 parts of Triton X-405. The plasticizer is at a level of 50% on the resin solids.

Table 11Caulk Emulsion Viscosity Response Data: Rhoplex 1785

Brookfield RVT Viscosities, RT, Pa.s	
Initial	
2.5 RPM	20
20 RPM	7
One hour	
2.5 RPM	26
20 RPM	8
Two hours	
2.5 RPM	29
20 RPM	8
24 Hours	
2.5 RPM	44
20 RPM	12
3 Days	
2.5 RPM	34
20 RPM	10

Note: Viscosity of neat emulsion is 0.6 Pa.s @ 2.5 RPM and 0.3 Pa.s @ 20 RPM. With the X-405 it is 1 Pa.s @ 2.5 RPM and 3 Pa.s @ 20 RPM's.

Table 12
Latex Caulk Formulation

Raw Material	Manufacturer	Pounds	Kg	Gallons	Litres
RHOPLEX 1785	Rohm & Haas	412.2	189.2	46.73	176.9
Water		26.9	12.2	3.23	12.2
Triton X-405	Rohm & Haas	9.2	4.17	1	3.7
Ethylene Glycol	Union Carbide	12.5	5.67	1.35	5.11
Tamol 850	Rohm & Haas	1.2	0.56	0.12	0.45
Thickener Natrosol (R) 250 MXR	Hercules	1	0.45	0.09	0.34
Dispersant, K TPP	Calgon	1	0.45	0.05	0.19
Blend B	Present Invention	114.7	52.0	13.82	52.31
Mineral Sprirts, Varsol (R) #1	Exxon	20	9.1	3.05	11.6
Adhesion Promoter, Silane Z-6040	Dow Corning	0.57	0.26	0.06	0.23
Extender, Calcium Carbonate, Drikilite(R)	E.C.C	735	333.3	32.6	123

Raw Material	Manufacturer	Pounds	Gallons
Pigment, Titanium Dioxide, TiPure R-901	Dupont	10	0.3
Ammonium Hydroxide, 28%	Fisher	3.5	0.39
Total		1352.77	102.79

Note: Rohm & Haas formulation AS-85-1 used.

Table 13
Caulk Package Stability and Viscosity Data

Test Parameter	
Initial Viscosity, Brookfield HAT, Helipath, RT, Pa.s	
1 Day	2300
7 Day	2700
Gunability, ASTM C-731	
1 Day, g/sec, RT	6.7
7 Day, g/sec., RT	5.5
28 Day, g/sec, RT	2.4
After 28 Days at 50°C	2.6
After 5 cycles F/T	3.1

Table 14
Physical Properties of Caulk

Property	
Low Temp. Flex., 1" mandrel	
@ -24° C	Pass
Shore A, 3 Week @ RT	
Initial, 1 sec	23
10 sec.	13
Tensile, ASTM D-638	
Maximum stress, psi	43, (1)
Elongation, %	680
180° Peel Adhesion, U.S. 230 Specification test	
Aluminum	
Lb/linear inch	6.5, (1.6)
Failure mode	CP/C
Wood, Ponderosa Pine	
Lb/linear inch	10.1 (2.4)
Failure mode	A/C
Wood Channel Crack	None
Tack Free Time, min.	9
Completion of Cure, days	7

Example 4**Latex Adhesive Applications**

[0043] A latex adhesive is used to adhere a porous substrate to another porous or a non porous substrate. Latex adhesives are used in a large variety of applications from paper and paperboard packaging to use to glue wood furniture. A latex adhesive may consist of only a polymeric binder, but in most instances other polymer modifiers are used to formulate an adhesive for a specific purpose. In most instances a plasticizer is used to formulate an adhesive based on homopolymers such as polyvinyl acetate, but are just as often are used to modify copolymer-based adhesives. An effective, compatible plasticizer is used in a latex adhesive to thicken the base emulsion (viscosity response), to increase flexibility, to reduce glass transition temperature, improve adhesions and low temperature performance, extend open time, shorten set time and reduce heat seal temperature. A blend of diethylene glycol dibenzoate, triethylene glycol dibenzoate and dipropylene glycol dibenzoate in the weight ratio of 1 to 0.5 to 0.5 (blend C) was incorporated in latex adhesive formulations based on both homopolymer and copolymer emulsions to assess the utility of plasticizers containing the present liquid ester blends for this application.

[0044] To function properly a plasticizer must be compatible with the base polymer. To determine the compatibility of blend C with adhesive polymers, adhesives based on a polyvinyl acetate homopolymer and a vinyl acetate/ethylene copolymer were prepared. The formulations are listed in Table 15, and the adhesives were prepared by stirring the plasticizer into the base emulsions. To test the compatibility of the plasticizer, a six mil-thick film of each adhesive was applied to glass plates using a draw down bar and dried for twenty four hours. All the films were clearer than the base emulsion and free of plasticizer exudation, indicating compatibility at the level of plasticizer tested.

[0045] The adhesive performance data are also listed in Table 15.

[0046] The emulsion viscosity response, open time, set time and caulk performance data indicate that mixture c of the present invention functions well as an adhesive plasticizer.

Table 15

Adhesive Formulations and Performance Data				
Formulation	1	2	3	4
Ingredient				
Vinac(R)XX-230 (Homopolymer)	100	89.5		
Airflex(R) 300 (Copolymer)			100	89.5
Blend C		10.5		10.5
Data				
Plasticizer compatibility				
Vinac(R) XX-230 Dry film appearance, after 24 hours	Very Hazy	Very Slight Haze	Very Hazy	Very Slight Haze
Plasticizer viscosity response				
Viscosity after 1 hour of preparation (ASTM D-1824)				
2.5 RPM's, Pa.s	4	5.8	4	19
20 RPM's, Pa.s	2.6	3.8	2	10
Viscosity after 24 Hours				
2.5 RPM's, Pa.s	4	5	4	20

EP 1 000 009 B1

Table 15 (continued)

Adhesive Formulations and Performance Data				
Formulation	1	2	3	4
Data				
Plasticizer compatibility				
20 RPM's, Pa.s	2.6	3.3	2	11
Set time, seconds	15	10	13	8
Open time, seconds	< 10	33	8	23
Adhesions, Visual rating with 0=none and 10=Complete bonding, to paper coated with:				
X-300	0	0	----	---
Nomar(R) 70	5	9	----	---

Example 5

[0047] Blends of diethylene glycol dibenzoate, triethylene glycol dibenzoate, and a third plasticizer were prepared and tested in the following manner. A glass vial was filled with 10 grams of test material and placed in a freezer at -12°C for 24 hours. After 24 hours, the vials were examined for signs of crystallization. The results are in Table 16. Samples were rated as a 'Pass' if there were no signs of crystallization.

Table 16

Weight percent in Blend					Rating
DOA ¹	DOP ²	DPGDB ³	DEGDB ⁴	TEGDB ⁵	
0	0	50	25	25	pass
0	50	0	25	25	pass
50	0	0	25	25	pass

1.) DOA is di-2-ethylhexyl adipate.

2.) DOP is di-2-ethylhexyl phthalate.

3.) DPGDB is dipropylene glycol dibenzoate.

4.) DEGDB is diethylene glycol dibenzoate.

5.) TEGDB is triethylene glycol dibenzoate.

[0048] The third plasticizer acts as a freeze point depressant for the two solid eaters and extends the useful range of the present compositions.

Claims

1. A liquid ester composition comprising a mixture of:

1) a first diester of the formula $\text{ArC(O)(OCH}_2\text{CH}_2)_2\text{O(O)CAr}$; and

2) a second diester of the formula $\text{ArC(O)(OCH}_2\text{CH}_2)_3\text{O(O)CAr}$;

wherein Ar represents a phenyl or methylphenyl radical, the weight ratio of said first diester to said second diester is from 1.22:1 to 9:1 and the freezing point of said mixture is below the freezing points of said first and second diesters.

2. A composition according to claim 1, wherein Ar represents a phenyl radical.

3. A liquid ester composition comprising a mixture of:

- 1) a first diester of the formula $\text{ArC(O)(OCH}_2\text{CH}_2)_2\text{O(O)CAr}$;
- 2) a second diester of the formula $\text{ArC(O)(OCH}_2\text{CH}_2)_3\text{O(O)CAr}$; and
- 3) at least one additional ester which is liquid at 25°C;

wherein Ar represents a phenyl or methylphenyl radical, the weight ratio of said first diester to said second diester is from 0.5:1 to 9:1, the freezing point of said mixture is below the freezing points of said first and second diesters, and wherein the combined weights of said first and second diesters constitute at least 50 weight percent of said composition.

4. A composition according to claim 3, wherein said additional ester is at least one member selected from the group consisting of 1) diesters derived from benzoic acid and diols containing from 3 to 10 carbon atoms, 2) esters derived from benzoic acid and monohydric alcohols containing from 4 to 12 carbon atoms, 3) aliphatic esters of the formula $\text{R}^1\text{O(O)C(CH}_2)_m\text{C(O)OR}^1$, wherein each R^1 is an alkyl radical individually selected from the group consisting of alkyl radicals containing from 8 to 12 carbon atoms, and m represents an integer from 2 to 8, and 4) esters derived from phthalic acid and alcohols containing from 4 to 12 carbon atoms, and wherein the combined weight of additional esters constitutes from 10 to 35 weight percent of said composition.

5. A composition according to claim 4, wherein said additional esters are selected from the group consisting of di (2-ethylhexyl) adipate and di(2-ethylhexyl) phthalate, and dipropylene glycol dibenzoate.

6. An organic polymer composition comprising at least one thermoplastic organic polymer and an amount sufficient to plasticize said polymer of a liquid ester composition comprising a mixture of:

- 1) a first diester of the formula $\text{ArC(O)(OCH}_2\text{CH}_2)_2\text{O(O)CAr}$ and
- 2) a second diester of the formula $\text{ArC(O)(OCH}_2\text{CH}_2)_3\text{O(O)CAr}$;

wherein Ar represents a phenyl or methylphenyl radical, the weight ratio of said first diester to said second diester is from 1.22:1 to 9:1 and the freezing point of said mixture is below the freezing points of said first and second diesters.

7. A composition according to claim 6, wherein Ar represents a phenyl radical.

8. An organic polymer composition comprising at least one thermoplastic organic polymer and an amount sufficient to plasticize said polymer of a liquid ester composition comprising a mixture of:

- 1) a first diester of the formula $\text{ArC(O)(OCH}_2\text{CH}_2)_2\text{O(O)CAr}$;
- 2) a second diester of the formula $\text{ArC(O)(OCH}_2\text{CH}_2)_3\text{O(O)CAr}$; and
- 3) at least one additional ester which is liquid at 25°C;

wherein Ar represents a phenyl or methylphenyl radical, the weight ratio of said first diester to said second diester is from 0.5:1 to 9:1, the freezing point of said mixture is below the freezing points of said first and second diesters, and wherein the combined weights of said first and second diesters constitute at least 50 weight percent of said liquid ester composition.

9. A composition according to claim 8, wherein said additional ester is at least one member selected from the group consisting of 1) diesters derived from benzoic acid and diols containing from 3 to 10 carbon atoms, 2) esters derived from benzoic acid and monohydric alcohols containing from 4 to 12 carbon atoms, 3) aliphatic esters of the formula $\text{R}^1\text{O(O)C(CH}_2)_m\text{C(O)OR}^1$, wherein each R^1 is an alkyl radical individually selected from the group consisting of alkyl radicals containing from 8 to 12 carbon atoms, and m represents an integer from 2 to 8, and 4) esters derived from phthalic acid and alcohols containing from 4 to 12 carbon atoms, wherein the combined weight of additional esters constitutes from 10 to 35 weight percent of said composition.

10. A composition according to 9 wherein said additional esters are selected from the group consisting of di (2-ethylhexyl) adipate and di (2-ethylhexyl) phthalate, and dipropylene glycol dibenzoate.

11. A composition according to claim 6 wherein the organic polymer is selected from the group consisting of polyvinyl chlorine and copolymers derived from vinyl chloride and at least one additional copolymerizable olefinically unsaturated compounds selected from the group consisting of vinylidene chloride, vinyl esters of carboxylic acids, and esters of ethylenically unsaturated carboxylic acids.

12. The composition according to claim 8 wherein the organic polymer is selected from the group consisting of polyvinyl chloride and copolymers derived from vinyl chloride and at least one additional copolymerizable olefinically unsaturated compounds selected from the group consisting of vinylidene chloride, vinyl esters of carboxylic acids, and esters of ethylenically unsaturated carboxylic acids.

13. The composition according to claim 11 wherein at least 70 percent of the repeating units of said copolymers are derived from the vinyl chloride.

14. The composition according to claim 12 wherein at least 70 percent of the repeating units of said copolymers are derived from vinyl chlorine

15. An adhesive composition comprising the polymer composition of claim 6.

16. An adhesive composition comprising the polymer composition of claim 8.

17. A latex caulk composition comprising the polymer composition of claim 6.

18. A latex caulk composition comprising the polymer composition of claim 8.

19. A liquid or solid coating composition comprising the polymer composition of claim 6.

20. A liquid or solid coating composition comprising the polymer composition of claim 8.

21. An oil composition containing as an additive the liquid composition of claim 1.

22. An oil composition containing as an additive the liquid composition of claim 3.

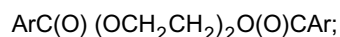
23. A lubricant composition containing as an additive the liquid composition of claim 1.

24. A lubricant composition containing as an additive the liquid composition of claim 3.

Patentansprüche

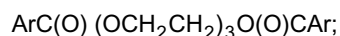
1. Flüssige Esterzusammensetzung, umfassend ein Gemisch aus:

1) einem ersten Diester der Formel



und

2) einem zweiten Diester der Formel

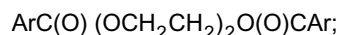


wobei Ar ein Phenyl- oder Methylphenylradikal repräsentiert, das Gewichtsverhältnis zwischen dem genannten ersten Diester und dem genannten zweiten Diester zwischen 1,22:1 und 9:1 liegt, und der Gefrierpunkt des genannten Gemischs unter dem Gefrierpunkt des genannten ersten und zweiten Diesters liegt.

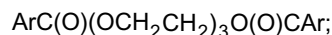
2. Zusammensetzung nach Anspruch 1, wobei Ar ein Phenylradikal repräsentiert.

3. Flüssige Esterzusammensetzung, umfassend ein Gemisch aus:

1) einem ersten Diester der Formel



2) einem zweiten Diester der Formel



und

3) wenigstens einem zusätzlichen Ester, der bei 25°C flüssig ist;

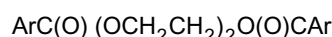
wobei Ar ein Phenyl- oder Methylphenylradikal repräsentiert, das Gewichtsverhältnis zwischen dem genannten ersten Diester und dem genannten zweiten Diester zwischen 0,5:1 und 9:1 liegt, der Gefrierpunkt des genannten Gemischs unter dem Gefrierpunkt des genannten ersten und zweiten Diesters liegt, und wobei die kombinierten Gewichte des genannten ersten und zweiten Diesters wenigstens 50 Gew.-% der genannten Zusammensetzung ausmachen.

4. Zusammensetzung nach Anspruch 3, wobei der genannte zusätzliche Ester wenigstens ein Mitglied der Gruppe ist, die aus Folgendem besteht: 1) Diester von Benzoesäure und Diolen mit 3 bis 10 Kohlenstoffatomen, 2) Ester von Benzoesäure und einwertigen Alkoholen mit 4 bis 12 Kohlenstoffatomen, 3) aliphatische Ester der Formel $\text{R}^1\text{O(O)C(CH}_2)_m\text{C(O)OR}^1$, wobei jedes R^1 ein Alkylradikal ist, das individuell ausgewählt ist aus der Gruppe bestehend aus Alkylradikalen mit 8 bis 12 Kohlenstoffatomen, und m eine ganze Zahl zwischen 2 und 8 repräsentiert, und 4) Ester von Phthalsäure und Alkoholen mit 4 bis 12 Kohlenstoffatomen, und wobei das kombinierte Gewicht zusätzlicher Ester zwischen 10 und 35 Gew.-% der genannten Zusammensetzung ausmacht.

5. Zusammensetzung nach Anspruch 4, wobei die genannten zusätzlichen Ester ausgewählt sind aus der Gruppe bestehend aus Di(2-ethylhexyl)adipat und Di(2-ethylhexyl)phthalat und Dipropylenglykoldibenzoat.

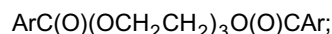
6. Organische Polymerzusammensetzung, die wenigstens ein thermoplastisches organisches Polymer und eine Menge umfasst, die ausreicht, um das genannte Polymer einer flüssigen Esterzusammensetzung zu plastifizieren, umfassend ein Gemisch aus:

1) einem ersten Diester der Formel



und

2) einem zweiten Diester der Formel

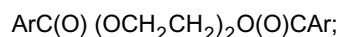


wobei Ar ein Phenyl- oder Methylphenylradikal repräsentiert, das Gewichtsverhältnis zwischen dem genannten ersten Diester und dem genannten zweiten Diester zwischen 1,22:1 und 9:1 liegt und der Gefrierpunkt des genannten Gemischs unter dem Gefrierpunkt des genannten ersten und zweiten Diesters liegt.

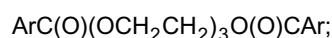
7. Zusammensetzung nach Anspruch 6, wobei Ar ein Phenylradikal repräsentiert.

8. Organische Polymerzusammensetzung, umfassend wenigstens ein thermoplastisches organisches Polymer und eine Menge, die ausreicht, um das genannte Polymer einer flüssigen Esterzusammensetzung zu plastifizieren, umfassend ein Gemisch aus:

1) einem ersten Diester der Formel



2) einem zweiten Diester der Formel



und

3) wenigstens einem zusätzlichen Ester, der bei 25°C flüssig ist;

wobei Ar ein Phenyl- oder Methylphenylradikal repräsentiert, das Gewichtsverhältnis zwischen dem genannten ersten Diester und dem genannten zweiten Diester zwischen 0,5:1 und 9:1 liegt, der Gefrierpunkt des genannten Gemischs unter dem Gefrierpunkt des genannten ersten und zweiten Diesters liegt, und wobei die kombinierten Gewichte des genannten ersten und zweiten Diesters wenigstens 50 Gew.-% der genannten flüssigen Esterzusammensetzung ausmachen.

9. Zusammensetzung nach Anspruch 8, wobei der genannte zusätzliche Ester wenigstens ein Mitglied der Gruppe ist, die aus Folgendem besteht: 1) Diester von Benzoesäure und Diolen mit 3 bis 10 Kohlenstoffatomen, 2) Ester von Benzoesäure und einwertigen Alkoholen mit 4 bis 12 Kohlenstoffatomen, 3) aliphatische Ester der Formel $\text{R}^1\text{O(O)C(CH}_2)_m\text{C(O)OR}^1$, wobei jedes R^1 ein Alkylradikal ist, das individuell ausgewählt ist aus der Gruppe bestehend aus Alkylradikalen mit 8 bis 12 Kohlenstoffatomen, und m eine ganze Zahl zwischen 2 und 8 repräsentiert, und 4) Ester von Phthalsäure und Alkoholen mit 4 bis 12 Kohlenstoffatomen, wobei das kombinierte Gewicht zusätzlicher Ester zwischen 10 und 35 Gew.-% der genannten Zusammensetzung ausmacht.

10. Zusammensetzung nach 9, wobei die genannten zusätzlichen Ester ausgewählt sind aus der Gruppe bestehend aus Di (2-ethylhexyl)adipate und Di (2-ethylhexyl)phthalat und Dipropylenglykoldibenzoat.

11. Zusammensetzung nach Anspruch 6, wobei das organische Polymer ausgewählt ist aus der Gruppe bestehend aus Polyvinylchlorid und Copolymeren von Vinylchlorid und wenigstens einer zusätzlichen copolymerisierbaren olefinisch ungesättigten Verbindung, ausgewählt aus der Gruppe bestehend aus Vinylidenchlorid, Vinylester von Carbonsäuren und Ester von ethylenisch ungesättigten Carbonsäuren.

12. Zusammensetzung nach Anspruch 8, wobei das organische Polymer ausgewählt ist aus der Gruppe bestehend aus Polyvinylchlorid und Copolymeren von Vinylchlorid und wenigstens einer zusätzlichen copolymerisierbaren olefinisch ungesättigten Verbindung, ausgewählt aus der Gruppe bestehend aus Vinylidenchlorid, Vinylester von Carbonsäuren und Ester von ethylenisch ungesättigten Carbonsäuren.

13. Zusammensetzung nach Anspruch 11, wobei wenigstens 70 Prozent der Wiederholungseinheiten der genannten Copolymere von Vinylchlorid abstammen.

14. Zusammensetzung nach Anspruch 12, wobei wenigstens 70 Prozent der Wiederholungseinheiten der genannten Copolymere von Vinylchlorid abstammen.

15. Klebstoffzusammensetzung, umfassend die Polymerzusammensetzung aus Anspruch 6.

16. Klebstoffzusammensetzung, umfassend die Polymerzusammensetzung aus Anspruch 8.

17. Latexdichtungszusammensetzung, umfassend die Polymerzusammensetzung aus Anspruch 6.

18. Latexdichtungszusammensetzung, umfassend die Polymerzusammensetzung aus Anspruch 8.

19. Flüssige oder feste Beschichtungszusammensetzung, umfassend die Polymerzusammensetzung aus Anspruch 6.

20. Flüssige oder feste Beschichtungszusammensetzung, umfassend die Polymerzusammensetzung aus Anspruch 8.

21. Ölzusammensetzung, die als einen Zusatz die flüssige Zusammensetzung aus Anspruch 1 enthält.

22. Ölzusammensetzung, die als einen Zusatz die flüssige Zusammensetzung aus Anspruch 3 enthält.

23. Schmiermittelzusammensetzung, die als einen Zusatz die flüssige Zusammensetzung aus Anspruch 1 enthält.

5 24. Schmiermittelzusammensetzung, die als einen Zusatz die flüssige Zusammensetzung aus Anspruch 3 enthält.

Revendications

10 1. Composition d'esters liquide comprenant un mélange de :

1) un premier diester de la formule

15
$$\text{ArC(O)(OCH}_2\text{CH}_2)_2\text{O(O)CAr ;}$$

et

2) un deuxième diester de la formule

20
$$\text{ArC(O)(OCH}_2\text{CH}_2)_3\text{O(O)CAr ;}$$

où Ar représente un radical phényle ou méthylphényle, le rapport de poids dudit premier diester audit deuxième diester est de 1,22:1 à 9:1, et le point de congélation dudit mélange est inférieur aux points de congélation desdits premier et deuxième diesters.

2. Composition selon la revendication 1, dans laquelle Ar représente un radical phényle.

30 3. Composition d'esters liquide comprenant un mélange de :

1) un premier diester de la formule

35
$$\text{ArC(O)(OCH}_2\text{CH}_2)_2\text{O(O)CAr ;}$$

et

2) un deuxième diester de la formule

40
$$\text{ArC(O)(OCH}_2\text{CH}_2)_3\text{O(O)CAr ;}$$

et

3) au moins un ester supplémentaire qui est liquide à 25°C ;

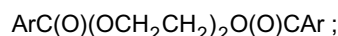
45 où Ar représente un radical phényle ou méthylphényle, le rapport de poids dudit premier diester audit deuxième diester est de 0,5:1 à 9:1, le point de congélation dudit mélange est inférieur aux points de congélation desdits premier et deuxième diesters, et où les poids combinés desdits premier et deuxième diesters constituent au moins 50% en poids de ladite composition.

50 4. Composition selon la revendication 3, dans laquelle ledit ester supplémentaire est au moins un élément sélectionné dans le groupe comprenant 1) des diesters dérivés de l'acide benzoïque et des diols contenant de 3 à 10 atomes de carbone, 2) des esters dérivés de l'acide benzoïque et des alcools monhydriques contenant de 4 à 12 atomes de carbone, 3) des esters aliphatiques de la formule $\text{R}^1\text{O(O)C(CH}_2)_m\text{C(O)OR}^1$, où chaque R^1 est un radical alkyle sélectionné individuellement dans le groupe comprenant des radicaux alkyle contenant de 8 à 12 atomes de carbone, et m représente un nombre entier de 2 à 8, et 4) des esters dérivés de l'acide phtalique et des alcools contenant de 4 à 12 atomes de carbone, et dans laquelle le poids combiné des esters supplémentaires constitue de 10 à 35% en poids de ladite composition.

5. Composition selon la revendication 4, dans laquelle lesdits esters supplémentaires sont sélectionnés dans le groupe comprenant le di(2-éthylhexyl)adipate et le di(2-éthylhexyl)phtalate, et le dibenzoate de dipropylène glycol.

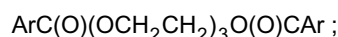
6. Composition polymère organique comprenant au moins un polymère organique thermoplastique et une quantité suffisante pour plastifier ledit polymère d'une composition d'esters liquides comprenant un mélange de :

1) un premier diester de la formule



et

2) un deuxième diester de la formule

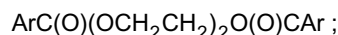


où Ar représente un radical phényle ou méthylphényle, le rapport de poids dudit premier diester audit deuxième diester est de 1,22:1 à 9:1, et le point de congélation dudit mélange est inférieur aux points de congélation desdits premier et deuxième diesters.

7. Composition selon la revendication 6, dans laquelle Ar représente un radical phényle.

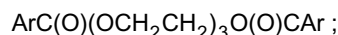
8. Composition polymère organique comprenant au moins un polymère organique thermoplastique et une quantité suffisante pour plastifier ledit polymère d'une composition d'esters liquides comprenant un mélange de :

1) un premier diester de la formule



et

2) un deuxième diester de la formule



et

3) au moins un ester supplémentaire qui est liquide à 25°C ;

où Ar représente un radical phényle ou méthylphényle, le rapport de poids dudit premier diester audit deuxième diester est de 0,5:1 à 9:1, le point de congélation dudit mélange est inférieur aux points de congélation desdits premier et deuxième diesters, et où les poids combinés desdits premier et deuxième diesters constituent au moins 50% en poids de ladite composition d'esters liquides.

9. Composition selon la revendication 8, dans laquelle ledit ester supplémentaire est au moins un élément sélectionné dans le groupe comprenant 1) des diesters dérivés de l'acide benzoïque et des diols contenant de 3 à 10 atomes de carbone, 2) des esters dérivés de l'acide benzoïque et des alcools monhydriques contenant de 4 à 12 atomes de carbone, 3) des esters aliphatiques de la formule $\text{R}^1\text{O(O)C(CH}_2)_m\text{C(O)OR}^1$, où chaque R^1 est un radical alkyle sélectionné individuellement dans le groupe comprenant des radicaux alkyle contenant de 8 à 12 atomes de carbone, et m représente un nombre entier de 2 à 8, et 4) des esters dérivés de l'acide phtalique et des alcools contenant de 4 à 12 atomes de carbone, et dans laquelle le poids combiné des esters supplémentaires constitue de 10 à 35% en poids de ladite composition.

10. Composition selon la revendication 9, dans laquelle lesdits esters supplémentaires sont sélectionnés dans le groupe comprenant le di(2-éthylhexyl)adipate et le di(2-éthylhexyl)phtalate, et le dibenzoate de dipropylène glycol.

11. Composition selon la revendication 6 dans laquelle le polymère organique est sélectionné dans le groupe com-

prenant le chlore de polyvinyle et les copolymères dérivés du chlorure de vinyle et au moins un composé oléfinique non saturé copolymérisable supplémentaire sélectionné dans le groupe comprenant le chlorure de vinylidène, les esters vinyliques d'acides carboxyliques, et les esters d'acides carboxyliques éthyléniques non saturés.

- 5 **12.** La composition selon la revendication 8 dans laquelle le polymère organique est sélectionné dans le groupe comprenant le chlorure de polyvinyle et les copolymères dérivés du chlorure de vinyle et au moins un composé oléfinique non saturé copolymérisable supplémentaire sélectionné dans le groupe comprenant le chlorure de vinylidène, les esters vinyliques d'acides carboxyliques, et les esters d'acides carboxyliques éthyléniques non saturés.
- 10 **13.** La composition selon la revendication 11, dans laquelle au moins 70% des unités récurrentes desdits copolymères sont dérivées du chlorure de vinyle.
- 14.** La composition selon la revendication 12, dans laquelle au moins 70% des unités récurrentes desdits copolymères sont dérivées du chlore de vinyle.
- 15 **15.** Composition adhésive comprenant la composition polymère de la revendication 6.
- 16.** Composition adhésive comprenant la composition polymère de la revendication 8.
- 20 **17.** Composition de calfeutrage au latex comprenant la composition polymère de la revendication 6.
- 18.** Composition de calfeutrage au latex comprenant la composition polymère de la revendication 8.
- 19.** Composition de revêtement liquide ou solide comprenant la composition polymère de la revendication 6.
- 25 **20.** Composition de revêtement liquide ou solide comprenant la composition polymère de la revendication 8.
- 21.** Composition d'huile contenant comme additif la composition liquide de la revendication 1.
- 30 **22.** Composition d'huile contenant comme additif la composition liquide de la revendication 3.
- 23.** Composition lubrifiante contenant comme additif la composition liquide de la revendication 1.
- 24.** Composition lubrifiante contenant comme additif la composition liquide de la revendication 3.